

AP/CPW



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Inventor/Appellant: Partho Sarkar

Title: CRACK-RESISTANT ANODE-SUPPORTED FUEL CELL

Application No. 10/658,803

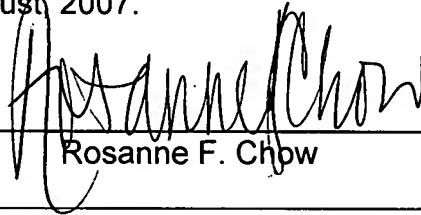
Filed: September 9, 2003

Examiner/Art Unit: ALEJANDRO, Raymond / 1745

Attorney File No.: 2281-001-03

CERTIFICATE OF MAILING OR TRANSMISSION

I hereby certify that this correspondence is being deposited in the United States Postal Service as First Class Mail in an envelope addressed to: Mail Stop Appeal Brief – Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on this 31st day of August 2007.



Rosanne F. Chow

RESPONSE TO NOTIFICATION OF NON-COMPLIANT APPEAL BRIEF

Dear Commissioner for Patents:

In response to a Notification of Non-Compliant Appeal Brief mailed July 31, 2007 in the above-referenced patent application, an amended appeal brief is hereby submitted. Changes to the Appeal Brief filed on February 8, 2007 that are contained in the amended appeal brief are shown in the enclosed redlined version.

//

//

Please contact the undersigned at 425-455-5575 if with any questions or comments regarding this matter. If the Patent Office finds that any fees are due, please charge any additional fees or credit overpayment to Deposit Account No. 07-1897.

Dated: August 31, 2007

Respectfully submitted,



Paul F. Rusyn
Attorney for Applicant
Registration No. 42,118
155-108th Avenue N.E., Ste. 350
Bellevue, WA 98004-5973
(425) 455-5575

Enclosures:

Copy of Notification of Non-Compliant Appeal Brief dated July 31, 2007
Redlined version of Revised Appeal Brief dated August 31, 2007
Accepted version of Revised Appeal Brief dated August 31, 2007
Return Postcard



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Inventor/Appellant: Partho Sarkar

Title: CRACK-RESISTANT ANODE-SUPPORTED FUEL CELL

Application No. 10/658,803

Filed: September 9, 2003

Examiner/Art Unit: ALEJANDRO, Raymond / 1745

Attorney File No.: 2281-001-03

CERTIFICATE OF MAILING OR TRANSMISSION

I hereby certify that this correspondence is being deposited in the United States Postal Service as First Class Mail in an envelope addressed to: Mail Stop Appeal Brief – Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on this 31st day of August, 2007.


Rosanne F. Chow

APPEAL BRIEF

Dear Commissioner for Patents:

This is an appeal pursuant to 37 C.F.R. § 1.191(a) from the decision of the Examiner, dated June 5, 2006, finally rejecting claims 1-12 of the above-referenced patent application. A request for a one-month extension of time is enclosed pursuant to 37 C.F.R. 1.36(a).

Attached to this Brief as **Appendix A** is a claims appendix containing a copy of all the claims involved in the Appeal, as required under 37 C.F.R. §41.37(a)(viii). An evidence appendix as required under 37 C.F.R. §41.37(a)(ix) accompanies this Brief in the form of **Appendices B-E**. **Appendix B** contains pages from a publication that illustrates the oxygen ion conduction and high electrical conductivity characteristics of the solid electrolyte yttria stabilized zirconia ("YSZ") that make YSZ suitable for use in

the anode support layer of a solid oxide fuel cell ("SOFC"). **Appendix C** contains pages from a publication illustrating the relatively high electrical resistivity of alumina (aluminum oxide). **Appendix D** contains pages from a publication further discussing desirable characteristics of solid electrolytes suitable for use in SOFCs. **Appendix E** lists several Web sites that contain exemplary information illustrating the characterization and use of alumina as an insulator.

The objective evidence that accompanies this brief as **Appendices B-E** was made of record in the Response to final Office Action filed on October 11, 2006. This evidence was submitted after the final Office Action because this was when the Examiner first requested such evidence (See page of the Interview Summary mailed September 12, 2006). Thus, this evidence was necessary to fully respond to the Examiner's request and could not have been earlier presented since such a request had not been made until that point in the prosecution of the present application. These are certainly good and sufficient reasons pursuant to 37 C.F.R. § 1.116(e) and this evidence is therefore of record in the present application in accordance with 37 C.F.R. §41.37(c)(2).

A related proceedings appendix as required under 37 C.F.R. §41.37(c)(1)(ii) accompanies this brief as **Appendix F** and indicates there are no related appeals, interferences, or judicial proceedings, as is discussed in more detail in Section II below.

I. *Real Party In Interest*

The real party in interest is Alberta Research Council, Inc., having a principal place of business at 250 Karl Clark Road, Edmonton, Alberta T6N 1E4, Canada. The inventors assigned this application to Alberta Research Council, Inc. ("Assignee") in an Assignment recorded on February 9, 2004 at reel no. 014958, frame no. 0347.

II. *Related Appeals and Interferences*

Based on information obtained from Alberta Research Council, Inc., and based on information and belief of the undersigned attorney, there are no prior or pending

appeals, interferences, or judicial proceedings known to Appellant, Appellant's legal representative the undersigned attorney, or the Assignee, which are related to, which directly affect or which will be directly affected by, or which have a bearing on the decision of the Board of Patent Appeals and Interferences ("the Board") in the pending Appeal. There are no such appeals, interferences, or judicial proceedings as indicated in the related proceedings appendix that accompanies this brief as **Appendix F**.

III. Status of Claims

Claims 1-13 are pending and stand rejected by the Examiner. Claims 1-12 are appealed.

IV. Status of Amendments

An Amendment After Final was filed on October 11, 2006 in response to a Final Office Action mailed on June 5, 2006. In an Advisory Action mailed on October 17, 2006, the Examiner indicated the proposed amendments in the Amendment After Final would not be entered as raising new issues that would require further consideration and/or search. **Appendix A** includes all the appealed claims 1-12 as they are currently pending.

V. Summary of Claimed Subject Matter

This summary of the invention provides cross-referencing to the application as required by 37 C.F.R. § 41.37(c)(v). This cross-referencing is solely to assist the Board in understanding the Applicant's invention and is not meant to be exhaustive or to limit the scope of the pending claims.

Independent claim 1 recites an anode-supported solid oxide fuel cell including an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. An electrolyte layer is in adjacent intimate contact with the anode support layer and a cathode layer is in adjacent intimate contact with the electrolyte layer.

Figure 1 illustrates a planar anode-supported solid oxide fuel cell 2 corresponding to one embodiment of present invention covered by claim 1. The anode-supported solid oxide fuel cell recited in claim 1 corresponds to the fuel cell 2 in the embodiment of Figure 2. See page 5, lines 25-30 and page 6, lines 1-3 (paragraph 16). The anode support layer recited in claim 1 corresponds to an anode support layer (ASL) 16 in the embodiment of the fuel cell 2 shown in Figure 2. *Id.* Claim 1 further recites that the anode support layer includes a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. This recited porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material is discussed on page 6, lines 16-30 and page 7, lines 1-2 (paragraph 19) with reference to the ASL 16. Claim 1 further recites an electrolyte layer that is in adjacent intimate contact with the anode support layer, where the recited electrolyte layer corresponds to an electrolyte layer 12 in the embodiment of Figure 1. *Id.* Finally, claim 1 recites a cathode layer that is in adjacent intimate contact with the electrolyte layer, where the recited cathode layer corresponds to a cathode layer 10 in the embodiment of Figure 2. *Id.*

Turning now to independent claim 12, this claim recites an anode-supported solid oxide fuel cell including a cathode layer in adjacent intimate contact with an electrolyte layer that is in adjacent intimate contact with an anode functional layer. The anode functional layer is in adjacent intimate contact with an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, with at least some of the vias being filled with electronically conductive material.

Claim 12 covers, for example, the embodiment of the present invention illustrated in Figure 2. The anode-supported solid oxide fuel cell recited in claim 12 corresponds to the fuel cell 2 in the embodiment of Figure 2. See page 8, lines 22-30 and page 9, lines 1-3 (paragraph 24). Claim 12 further recites that the fuel cell includes a cathode layer in adjacent intimate contact with an electrolyte layer that is in adjacent intimate contact with an anode functional layer. The recited cathode layer, electrolyte layer, and anode functional layer correspond to a cathode layer 10, electrolyte layer 12,

and anode functional layer 14, respectively, in the embodiment of Figure 2. Claim 12 further recites that the anode functional layer, which corresponds to layer 14 in Figure 2, is in adjacent intimate contact with an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, with at least some of the vias being filled with electronically conductive material. The recited anode support layer corresponds to the anode support layer 16 in the embodiment of Figure 2. *Id.* The recited plurality of vias extending through the thickness of the oxygen ion-conducting structure correspond to the vias 20 in the embodiment of Figure 2. *Id.*

VI. *Grounds of Rejection to Be Reviewed On Appeal*

- 1. Whether U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. (“Shibata”) anticipates claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e).**
- 2. Whether claims 7-8 and 10 are obvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al. (“Sammes”).**

VII. *Argument*

- 1. Claims 1-6, 9, and 11-12 are allowable under 35 U.S.C. § 102(e) over U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. (“Shibata”) because Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material.**

“Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim.” *Gechter v. Davidson*, 42

USPQ2d 1030, 1032 (Fed. Cir. 1997). Before determining whether a prior art reference anticipates a claim, one must first construe the claim “to define the scope and meaning of each contested limitation.” *Id.* The proper starting place in any claim construction analysis is the claim language itself read in view of the specification and the prosecution history. *Phillips v. AWH Corp.*, 415 F.3d 1303 (Fed. Cir. 2005) (*en banc*).

In the final Office Action mailed 5 June 2006, the Examiner maintained the rejections of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) as being anticipated by Shibata. On September 7, 2006, the undersigned along with the inventor Partho Sarkar and Brian Y. Lee, Canadian counsel for the Assignee, held a telephone interview with the Examiner to discuss the rejections of the pending claims (See the Examiner's Interview Summary mailed September 12, 2006 that is part of the file history of the present application). During this telephone interview, the Examiner construed the “porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material” recited in claim 1 as corresponding to the porous metallic base body 1 illustrated in Figures 4-7. Paragraph 44 of Shibata states “it may be possible for the porous metallic base body [1] to be made of a ceramic which is plated with the above metals [e.g., nickel Ni] or with the alloy containing the above metals.” Paragraph 69 more specifically provides “the porous base body 1 ... includes a ceramic (alumina) body plated with [nickel] Ni.” In both the final Office Action (Item 2, bottom of page 3) and during the telephone interview, the Examiner erroneously concluded that the alumina portion of the base body 1 corresponds to the “porous ion-conducting structure” and the nickel Ni coating corresponds to the “catalytic and electronically conductive material” as recited in claim 1.

Notwithstanding the Examiner's assertions, alumina is not a porous ion-conducting material. This fact is well understood and known by those skilled in the art. Alumina is an insulator having a resistivity that is too high for this material to be considered a solid electrolyte and an oxygen ion conductor suitable for use in a solid oxide fuel cell. In order for a material to be considered an oxygen ion conductor suitable for use in an electrode of a solid oxide fuel cell, the material must provide the necessary and efficient ionic path for anodic reaction which takes place during solid

oxide fuel cell operation. As is well known in the solid oxide fuel cell art, the ionic conductivity of the anode must be comparable to the ionic conductivity of the electrolyte. Moreover, alumina's resistivity is too high at the operating temperature of a solid oxide fuel cell to perform the required electrode function for the fuel cell.

During the Examiner interview, the Examiner contended that even if alumina is considered in the prior art as an insulating material this material is nonetheless capable of conducting some ions, even if such ion conductivity is poor. See page 3 of the Interview Summary. The Examiner requested objective evidence to support that such an alumina ceramic is "incapable" of transporting ions, meaning that the material exhibits no ion conduction at all. *Id.*

A suitable material for the recited anode support layer and thus an ion-conducting material is yttria stabilized zirconia (YSZ). See, e.g., paragraph 8 of the present application. YSZ is an excellent conductor of negatively charged oxygen (oxide) ions at high temperatures. See paragraph 3. A solid oxide fuel cell operates at an elevated temperature, typically on the order of between 700-1000 °C. *Id.* See page 101 of the Suresh publication that accompanies this amendment as **Appendix B** regarding general characteristics of ion-conducting materials. Other oxygen ion conducting materials suitable for use in a solid oxide fuel cell may be substituted for YSZ in the anode support layer. See paragraph 19. A characteristic of a solid electrolyte, which may otherwise be known as a fast ion conductor or a superionic solid, is a high electrical conductivity in the range of 10^{-1} - 10^{-4} ohm⁻¹cm⁻¹ (*i.e.* a resistivity of 10-10,000 ohm⁻¹cm⁻¹). See page 17 of **Appendix B**. In contrast, alumina (aluminum oxide) has a resistivity of 5.0×10^8 at 700°C and 2×10^6 at 1000°C (see page 959 of the Shackelford and Alexander publication, which accompanies this amendment as **Appendix C**. This large resistivity of alumina plainly evidences that alumina is not a solid electrolyte/fast ion conductor/superionic solid suitable for use in a solid oxide fuel cell. See the highlighted portions of the article that accompanies this amendment as **Appendix D** for additional information regarding desired resistivity values in fuel cells. **Appendix E** contains a listing of several Web sites that illustrate alumina being characterized and used as an insulator and not an ionic-conductor.

All the above evidence clearly demonstrates that the Examiner is in error in asserting that the alumina disclosed in Shibata corresponds to the recited porous ion-conducting material. Moreover, the Examiner's contention that because alumina must exhibit some ion conductivity the base body 1 of Shibata may be considered to correspond to the porous ion-conducting structure of the anode support layer recited in claim 1. Materials are classified as having physical characteristics that result in each material being placed in a particular class of materials, such as an electric or thermal conductor or insulator or an ionic conductor or insulator. Materials are not classified in absolute terms as would be required using the Examiner's logic. The Examiner requested evidence that "ceramic alumina is INCAPABLE of transporting ions (no ion conduction at all)." See page 3 of the Interview Summary. No such evidence can be provided for any material. Although classified as a particular type of material, every material will exhibit some characteristics of another class of materials. For example, materials classified as electrical insulators exhibit some amount of electrical conductivity, but such conductivity is so small that these materials are nonetheless classified as insulators. If the Examiner's argument was accepted, then the classification of materials would be rendered meaningless. Any material could be said to be whatever type of material was needed by an Examiner when formulating a rejection.

Pursuant to MPEP § 2111, during patent examination the pending claims must be given their broadest reasonable interpretation consistent with the specification. The Examiner expressly mentioned this well known tenet of patent examination during the Examiner interview. As expressly set forth in Section 2111, the "broadest reasonable interpretation of the claims must also be consistent with the interpretation that those skilled in the art would reach." As evidenced by the accompanying technical literature, one skilled in the art would not interpret the phrase "ion-conducting structure" to include the insulating material of alumina ceramic. The Examiner's attempt to so interpret this phrase is simply put an unreasonable interpretation of this language. Although the Examiner cites the "broadest reasonable interpretation" language of Section 2111 as the rationale for his interpretation, such an interpretation of this language plainly in violation of this section of the MPEP as well as in contravention of common sense.

For all these reasons, Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material as recited in claim 1. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer. As discussed above, an alumina ceramic simply is not “a porous ion-conducting structure.”

Because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. As previously discussed with reference to **Appendices B-E**, alumina’s resistivity is too high for this material to be considered a solid electrolyte and an ion conductor for a solid oxide fuel cell. Alumina’s resistivity is also too high at the operating temperatures of solid oxide fuel cells to carry out the required electrode function.

Furthermore, claim 1 recites an electrolyte layer in intimate contact with the anode support layer. Shibata discloses electrodes 10 and 11 to be in intimate contact with the electrolyte and not the base body 1 asserted by the Examiner to correspond to the anode support layer. Thus, claim 1 is allowable for this additional reason.

For all these reasons, the combination of elements recited in claim 1 is allowable and dependent claims 2-11 are allowable for at least the same reasons as claim 1 and due to the additional limitations added by each of these claims.

Claim 12 recites an anode-supported solid oxide fuel cell comprising an anode support layer including an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure. At least some of the vias are filled with electronically conductive material. An anode functional layer is in adjacent intimate contact with the anode support layer and an electrolyte layer is in adjacent intimate contact with the anode functional layer. A cathode layer is in adjacent intimate contact with the electrolyte layer.

Shibata neither discloses nor suggests an anode support layer as recited in claim 12. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer since an alumina ceramic is not an oxygen ion-conducting structure. Simply because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. Alumina’s resistivity is too

high for this material to be considered a solid electrolyte and an oxygen ion conductor for a solid oxide fuel cell and the resistivity is also too high at the operating temperatures to carry out the required electrode function.

For all these reasons, the combination of elements recited in claim 12 is allowable.

During the interview, the Examiner also raised what he termed a potential 35 U.S.C. § 112, paragraph 1, issue regarding the recitation of an ion-conducting structure in the claims and pointed to paragraph 19 of the specification to support his assertion that only a description of oxygen ion conducting materials is contained in the application. See page 3 of the Interview Summary. The Examiner states that “the invention, as presently claimed, may have a [Section] 112 issue (lack of adequate written support, and may be [sic] lack of enablement) because it clearly does not disclose, suggest or teach how “ANY” ion conducting material can be suitably used in the claimed anode structure.” While not at issue here a brief reply to this comment is provided. It is the Examiner and not the Applicant that is inserting the word “any” before the claim term “ion-conducting structure” recited in claims 1 and 12. Claim terms must be construed in the context of the application. As expressly noted by the Examiner on page 3 of the Interview Summary, the present application (paragraph 19, lines 4-7) states “other oxygen ion conducting materials suitable for SOFC use and having a relatively similar thermal coefficient to the electrolyte, as is known in the art, may be substituted for YSZ.” Claims 1 and 12 are directed to anode-supported solid oxide fuel cells. In the context of solid oxide fuel cells, one skilled in the art would understand the recited term “ion conducting structure” to relate to oxygen ions. No Section 112 issue exists.

- 2. Claims 7-8 and 10 are nonobvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al. (“Sammes”) since there is no disclosure or suggestion.**

In the final Office Action, the Examiner rejected claims 7, 8 and 10 under 35 U.S.C. § 103(a) as being obvious in view of Shibata and Sammes. As discussed

above, nothing in Shibata discloses or suggests the recited anode support layer. Furthermore, Sammes describes anode layers that comprise different ratios of electrochemically active substance. Sammes also describes a process for manufacturing a solid oxide fuel cell anode wherein YSZ powder is added to NiO powder and these materials are milled, extruded, dried and sintered together. As discussed above, one would expect a cross-sectional micrograph of the base body described in Sammes to reveal a porous structure comprising a homogenous composition within each layer. There is no suggestion in Sammes to impregnate catalytic and electronically conductive material into the pores of an anode support layer, thereby creating an anode support layer having a non-homogeneous porous structure.

Claim 7 recites the fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other. The recited porous structure is non-homogeneous in that the electronically conductive material of nickel Ni is compositionally graded through the thickness of the anode support layer. As a result, the anode support layer has a higher concentration of nickel Ni at one major surface than at the other major surface. Within the recited single anode support layer the electronically graded material is graded through the thickness of this single layer. Sammes discloses multiple layers with the concentration within each layer being homogeneous or constant and not graded. For these reasons, even if combined Shibata and Sammes do not teach or suggest the recited structure of claim 7. Claim 7 is accordingly allowable.

Claim 8 recites the fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material. Once again, Sammes neither discloses or suggest a single anode support layer having a nickel Ni concentration graded as recited in claim 7 and then a second conductive material concentrated at the major surface of the anode support layer having the lower

concentration of nickel Ni as recited in claim 8. Claim 8 is accordingly allowable for these additional reasons.

3. Dependent Claims Not Specifically Addressed In Section VIII

All dependent claims not specifically addressed in this section are patentable by virtue of their respective dependencies from claims for which the Applicants have presented an argument for patentability.

VIII. *Claims Appendix*

Appendix A includes all the appealed claims 1-12 as they are currently pending.

IX. *Evidence Appendix*

Appendices B through E include all objective evidence that was made of record in the Response to Final Office Action filed on October 11, 2006.

X. *Related Proceedings Appendix*

Appendix F indicates there are no related appeals, interferences, or judicial proceedings, as is discussed in more detail in Section II above.

XI. *Conclusion*

For the foregoing reasons, the Applicants request the Board to reverse the Examiner's rejection of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) and his rejection of claims 7, 8, and 10 under 35 U.S.C. § 103(a) and remand the application to the Examiner for issuance of claims 1-12.

//

//

//

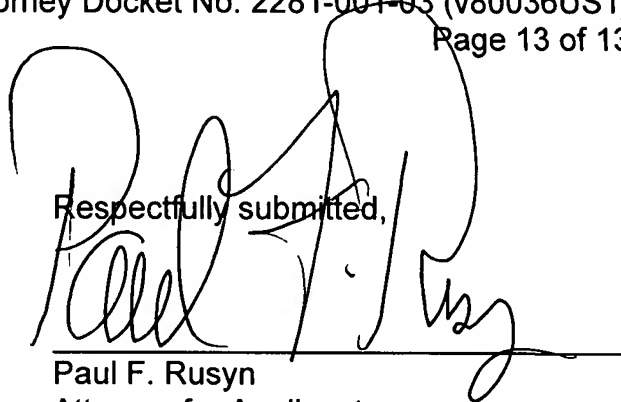
//

//

//

Dated: August 31, 2007

Respectfully submitted,



Paul F. Rusyn
Attorney for Applicant
Registration No. 42,118
155-108th Avenue N.E., Ste. 350
Bellevue, WA 98004-5973
(425) 455-5575

Enclosures:
Appendices A-F
Return Postcard



APPENDIX A

1. An anode-supported solid oxide fuel cell comprising
 - (a) an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material;
 - (b) an electrolyte layer in adjacent intimate contact with the anode support layer; and
 - (c) a cathode layer in adjacent intimate contact with the electrolyte layer.
2. The fuel cell of claim 1 wherein the catalytic and electronically conductive material is selected from the group of nickel, copper, silver, tungsten, and any alloys of these materials.
3. The fuel cell of claim 2 further comprising a second phase material mixed with the catalytic and electronically conductive material, the second phase material being selected from the group of yttria-stabilized zirconia (YSZ), doped cerium oxide, alumina or its salts.
4. The fuel cell of claim 2 further comprising an anode functional layer between the anode support layer and the electrolyte layer such that the electrolyte layer is in adjacent intimate contact with the anode functional layer instead of the anode support layer.
5. The fuel cell of claim 4 wherein the porous ion-conducting structure of the anode support layer is substantially yttria-stabilized zirconia (YSZ).

6. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is substantially evenly distributed throughout the anode support layer.
7. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other.
8. The fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material.
9. The fuel cell of claim 4 further comprising a porous zirconia-nickel cermet buffer layer sandwiched in between the anode support layer and anode functional layer, and having a porosity between 40-90%.
10. The fuel cell of claim 4 wherein the porous ion conducting structure of the anode support layer is comprised of a mixture of 10-30 vol. % of Ni, or NiO or both, and the balance yttria-stabilized zirconia (YSZ).
11. The fuel cell of claim 4 wherein the anode support layer further comprises a plurality of vias extending through the thickness of the ion conducting structure of the anode support layer, at least some of the vias being filled with an electronically conducting material.
12. An anode-supported solid oxide fuel cell comprising

- (a) an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, at least some of the vias being filled with electronically conductive material;
- (b) an anode functional layer in adjacent intimate contact with the anode support layer;
- (c) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
- (d) a cathode layer in adjacent intimate contact with the electrolyte layer.

13. An anode-supported solid oxide fuel cell comprising
- (a) an anode support layer;
 - (b) a porous cermet buffer layer in adjacent intimate contact with the anode support layer, and being composed of a zirconia-nickel cermet with a porosity between 40 and 90%;
 - (c) an anode functional layer in adjacent intimate contact with the buffer layer;
 - (d) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
 - (e) a cathode layer in adjacent intimate contact with the electrolyte layer.

APPENDIX B

*super-
ionic
solids*

PRINCIPLES
AND
APPLICATIONS

SURESH CHANDRA

*Professor of Physics,
Banaras Hindu University,
Varanasi, India*



NORTH-HOLLAND PUBLISHING COMPANY
AMSTERDAM · NEW YORK · OXFORD

CHAPTER 2

Superionic Materials and Structures

Superionic solids are ionic materials with high electrical conductivity comparable with those of liquid electrolytes. These materials are also termed "solid electrolytes" or "fast ion conductors". Typically a superionic solid has the following characteristics:

- (i) crystal bonding is ionic;
- (ii) electrical conductivity is high ($10^{-1} - 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$);
- (iii) principal charge carriers are ions which means that the ionic transference number (t_{ion}) is almost equal to 1 (here t_{ion} refers to the fractional contribution of the ionic conductivity to the total conductivity);
- (iv) the electronic conductivity is small; generally materials with electronic transference number (t_e) less than 10^{-4} are considered satisfactory superionic solids.

The values of electrical conductivity of a few ionic and superionic solids are shown in Figure 2.1. The highest conductivity at room temperature obtained so far is for RbAg_4I_5 which is $0.27 \text{ ohm}^{-1} \text{ cm}^{-1}$. This is many orders of magnitude higher than those of the more commonly known ionic solids KCl , NaCl etc, which have room temperature conductivity $\sim 10^{-12} - 10^{-16} \text{ ohm}^{-1} \text{ cm}^{-1}$. It may be noted that most of the superionic materials attain a high electrical conductivity above a certain temperature which may or may not be well defined. In other words, with increasing temperature the electrical conductivity sometimes changes gradually (as in β -alumina) or shows an abrupt jump (e.g. in β - AgI , RbAg_4I_5 etc.). Furthermore, for the latter materials the abrupt conductivity change is sometimes associated with a distinct structural change (like the $\beta \rightarrow \alpha$ transition in AgI) but sometimes this is not so clear (as in RbAg_4I_5). Structures which allow fast ion transport are generally disordered, "channelled" or "layered" (Wiedersich and Geller 1971). Ion-Ion interactions or correlation

over, Owens (1971) has noted that M^+ ions with volumes greater than $85(\text{\AA}^3)$ do not generally form conductive compounds. Furthermore, for bigger cations a lesser amount may be needed. For example, the maximum conductivity is obtained with 13 mole % MI for the $(\text{CH}_3)_4\text{NI}-\text{AgI}$ system, 12.5 mole % in the $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{NI}-\text{AgI}$ system and 12 mole % in the $(\text{C}_2\text{H}_5)_4\text{NI}-\text{AgI}$ system. This means that the percentage of added cations decreases with its increasing size as is expected from Raleigh's picture.

The above structural principles have been deduced on the basis of the very small amount of available structural data — mostly on cation substituted systems. More structural studies would be necessary both on anion and cation substituted systems to arrive at a better understanding.

2.8 Oxygen ion conductors

The first solid oxide electrolyte ever used was probably the ceramic with composition 85 wt % ZrO_2 , 15 wt % Y_2O_3 which was used by Nernst (1899) as an incandescent lighting material. Later Baur and Preis (1937) used this material for a fuel cell. The definite conductivity mechanism in terms of oxygen vacancies was proposed by Wagner (1943) and later verified by Hund (1952). However, the sudden increase of scientific interest in such materials started after Kiukola and Wagner (1957a, 1957b) illustrated their use in high-temperature thermodynamic measurements and fuel cells. In principle, almost all oxides can be expected to show some degree of oxygen ion conduction particularly the non-stoichiometric oxides. The non-stoichiometry can be created by heating the metal oxides in vacuum or oxygen or the relevant metallic vapour (Wagner 1974). Most of the oxygen ion conductors are good only at high temperatures ($\sim 1000^\circ\text{C}$) and are mixed conductors (ionic + electronic + electron-hole). As in the case of other ionic conductors, the conductivity in this case is strongly dependent on the temperature and doping with aliovalent impurities (like Ca^{2+} , Y^{3+} , Sr^{2+} etc. in HfO_2 , CeO_2 etc.) which control the number of point defects and their mobility. However, a unique property of oxide conductors is the dependence of the conductivity on the ambient pressure or activity. If the ambient oxygen pressure is low, the oxygen ions (O_O) would leave the solid electrolyte according to the following mechanism:

The defects are expressed in the Kröger-Vink notation: the symbol indicates the defect; the subscript the location of the defect; and the superscripts (') (.) denote negative and positive charges respectively. For example V_O^\bullet means vacancy at the oxygen site having effectively two positive charges. Similarly, O_i'' would indicate an oxygen ion at the interstitial site with effectively two negative charges.

tions, cooperative hopping or correlation effects play important roles. Details of the conductivity mechanism will be discussed in Chapter 4. Figure 2.46 gives a schematic plot of conductivity as a function of partial pressure of ambient oxygen for a typical oxide electrolyte at three different temperatures: The higher the temperature, the lower is the range of oxygen pressure over which the conductivity is ionic. The dependence of the range of ionic conduction on concentration of aliovalent dopant (like Ca^{2+} or Y^{3+}) is shown in Figure 2.47. The effect of increasing concentration is to broaden the range of ionic conductivity and shift the whole conductivity curve to lower p_{O_2} values.

Most of the useful oxide electrolytes developed so far are based on ThO_2 , CeO_2 , HfO_2 and zirconia, though some other systems have also been described. For an earlier review see Etsell and Flengas (1970). The common structure which sustains high oxygen ion conduction is the "fluorite structure". The fluorite structure for MO_2 (M = metal ion Th, Ce etc) is shown in Figure 2.48. In this structure there are a large number of octahedral interstitial voids. Each metal cation is surrounded by eight

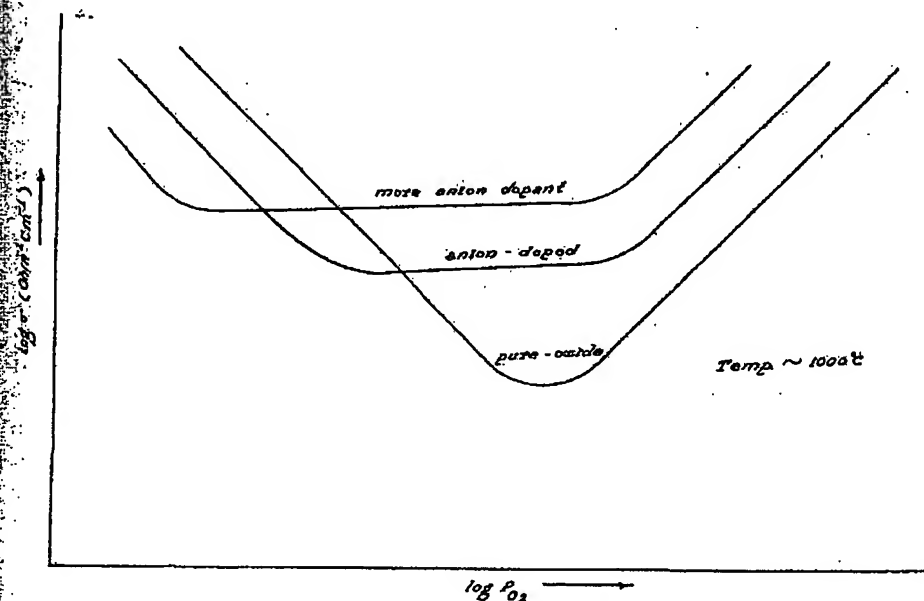


Fig. 2.47 Schematic representation of the dependence of conductivity of any oxide ion electrolyte on oxygen partial pressure for samples doped with different concentrations of aliovalent anion (Ca^{2+} , Y^{3+} etc.).

©North-Holland Publishing Company, 1981

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN: 0 444 86039 8

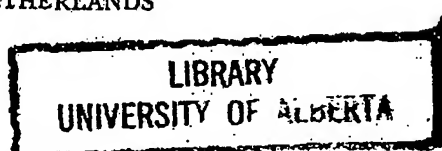
Publishers:

North-Holland Publishing Company—Amsterdam • New York • Oxford

Sole distributors for the U.S.A. and Canada:

Elsevier North-Holland, Inc. 52 Vanderbilt Avenue, New York, N.Y. 10017

PRINTED IN THE NETHERLANDS



CRC

**MATERIALS SCIENCE
AND
ENGINEERING
HANDBOOK**

THIRD EDITION

James F. Shackelford

Professor of Materials Science and Engineering
Division of Materials Science and Engineering
and
Associate Dean of the College of Engineering
University of California, Davis

William Alexander

Research Engineer
Division of Materials Science and Engineering
University of California, Davis



CRC Press

Boca Raton London New York Washington D C

Electrical Properties**Table 29I. RESISTIVITY OF CERAMICS**

(SHEET 4 OF 6)

Class	Ceramic	Resistivity (Ω -cm)	Temperature Range of Validity
Ic	Aluminum Oxide (Al_2O_3)	$>10 \times 10^{14}$	25°C
		2×10^{13}	100°C
		1×10^{13}	300°C
		6.3×10^{10}	500°C
		5.0×10^8	700°C
		2×10^6	1000°C
	Beryllium Oxide (BeO)	$>10^{17}$	25°C
		$>10^{15}$	300°C
		$1-5 \times 10^{15}$	500°C
		$1.5-2 \times 10^{15}$	700°C
		$4-7 \times 10^{15}$	1000°C
	Magnesium Oxide (MgO)	1.3×10^{15}	27°C
		$0.2-1 \times 10^8$	1000°C
		4×10^2	1727°C
	Silicon Dioxide (SiO_2)	10^{18}	room temp.
	Zirconium Oxide (ZrO_2)		
	(stabilized)	2300	700°C
	(stabilized)	77	1200°C
	(stabilized)	9.4	1300°C
	(stabilized)	1.6	1700°C
	(stabilized)	0.59	2000°C
	(stabilized)	0.37	2200°C

Compiled by J.S. Park from No. 1 Materials Index, Peter T.B. Shaffer, Plenum Press, (1964); Smithells Metals Reference Book, Eric A. Brandes, ed., in association with Research Institute Ltd. 6th ed. London, Butterworths, Boston, (1983); and Ceramic American Ceramic Society (1986-1991).

Library of Congress Cataloging-in-Publication Data

CRC materials science and engineering handbook / (edited by) James F. Shackelford,
William Alexander.—3rd ed.

p. cm.

Includes bibliographical references and index.

ISBN 0-8493-2696-6 (alk. paper)

1. Materials—Handbooks, manuals, etc. I. Shackelford, James F. II. Alexander,
William, 1950 Feb. 13.

TA403.4 .C74 2000
620.1'1—dc21

00-048567

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press LLC for such copying.

Direct all inquiries to CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton, Florida 33431.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe.

© 2001 by CRC Press LLC

No claim to original U.S. Government works

International Standard Book Number 0-8493-2696-6

Library of Congress Card Number 00-048567

Printed in the United States of America 1 2 3 4 5 6 7 8 9 0

Printed on acid-free paper

Materials for fuel-cell technologies

Brian C. H. Steele* & Angelika Heitmann†

*Centre for Ion Conducting Coatings, Department of Materials, Imperial College, London SW7 2BZ, UK (e-mail: b.steele@imperial.ac.uk)
†Fraunhofer Institute for Solar Energy Systems, Heilheiderstrasse 2, 79110 Freiburg, Germany
†Present address: Polytechnic Engineering School, University of Bath, Claverton Down, Bath BA2 9AY, UK (e-mail: a.heitmann@bath.ac.uk)

Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. However, before fuel-cell technology can gain a significant share of the electrical power market, important issues have to be addressed. These issues include optimal choice of fuel, and the development of alternative materials in the fuel-cell stack. Present fuel-cell prototypes often use materials selected more than 25 years ago. Commercialization aspects, including cost and durability, have revealed inadequacies in some of these materials. Here we summarize recent progress in the search and development of innovative alternative materials.

The successful conversion of chemical energy into electrical energy to a primitive fuel cell was first demonstrated¹ over 150 years ago. However, in spite of the attractive system efficiencies and environmental benefits associated with fuel-cell technology, it has proved difficult to develop the early scientific experiments into commercially viable industrial products. These problems have often been associated with the lack of appropriate materials or manufacturing routes that would enable the cost of electricity per kWh to compete with the existing technology, as outlined in a recent survey².

The types of fuel cells under active development are summarized in Fig. 1. The alkaline fuel cell (AFC), polymer-electrolyte-membrane fuel cell (PEMFC) and phosphoric-acid fuel cell (PAFC) stacks essentially require readily pure hydrogen to be supplied to the anode. Accordingly, the use of hydrogen or alcohol fuels requires an external fuel processor to be incorporated into the system. This format only increases the complexity and cost of the fuel cell. In contrast, solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs) operate at higher temperatures, such that the fuel can be reformed within the stack, which enables conversion thermal integration/management design features to provide cost-effective efficiencies (>50%).

Although the introduction of a 'hydrogen economy' might seem an attractive scenario, its implementation is least with formidable technical and economic difficulties. The clearest technology for the large-scale production of hydrogen is the steam reforming of natural gas, which produces significant emissions of greenhouse gases. The type of hydrogen storage is addressed in the accompanying review by Schabert and Zorzi (see pages 253–266); whilst there is a breakthrough in the production of hydrogen and the development of new hydrogen-storage materials, the concept of a 'hydrogen economy' will remain an unlikely scenario. In this article, therefore, we assume that fuel cells have to be designed for operation on hydrocarbon or alcohol fuels to ensure that the technology is able to penetrate the relevant major markets. Otherwise fuel-cell technology will be confined to restricted niche activities where hydrogen might be a convenient option, such as city bus fleets. Clearly the choice of fuel is a

further complication in the factors influencing the commercialization of fuel cells.

Constraints on material selection

Material selection for a commercial product involves an iterative design process that eventually focuses specifically on the particular product and application. However, it is possible to make a few general statements about the selection of materials for fuel cells. The required area-specific power (ASP) of the cell components (electrolyte, anode and cathode) should be between 0.5–2.0 W cm⁻² (area density approach) or 1.0–2.0 W cm⁻² (high power density, with length of 1 kW cm⁻² and 1 kW kg⁻¹ when mentioned for transport applications). High power densities are also important to reduce costs, as the amount of material per kW is then reduced. These topics, and considerations of cell efficiencies, are summarized in Box 1.

The need for reforming of hydrocarbon fuels is a major impact on the selection and processing of the cell components. Considerable development of porous electrode structures was achieved for the first time only about 40 years ago. The electrolyte, gaseous reactants, electrocatalyst and current collectors have to be brought into close contact within a confined porous structure. The porous structure is usually formed by hydrophobic polytetrafluoroethylene (PTFE or Teflon) greatly modified (the fabrication of porous, high-thermal-stability porous carbon papers) provided the electronic pathways, and to function as the electrolyte support. The electrolyte and current collectors were usually incorporated into the structure during the PTFE by dissolving small crystallites (2–5 nm) of the electrocatalyst (usually platinum or Pt alloys) onto carbon powder or paper. In retrospect, the assemblage of these components was probably the first manifestation of an engineered microstructure, and it is not surprising that its implementation more than 40 years ago was so difficult.

High ionic conductivities (>1 S cm⁻¹) associated with the liquid KOH, phosphoric acid and molten carbonate electrolytes ensured that, with appropriate design strategies, the ASP values of these components can be small. Although solid-state electrolytes have lower ionic conductivity values, the molten membranes used in the PEMFC system can be fabricated relatively easily as a thin film (100 nm) to produce satisfactory ASP values provided the water content of the film is controlled under the dynamic conditions of cell operation. In contrast, it has been, and continues to be,

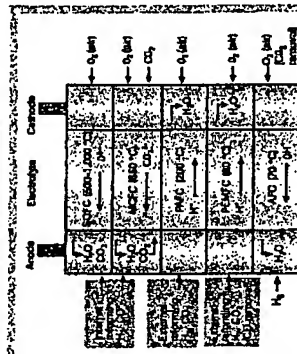


Figure 1. Schematic diagram of a fuel cell system. The fuel cell system consists of a fuel cell, a fuel supply, an oxidant supply, and a water management system. The fuel cell is the central component, where the electrochemical reaction takes place. The fuel supply provides the fuel (H₂ or CH₃OH) to the anode, and the oxidant supply provides the oxidant (O₂) to the cathode. The water management system ensures that the fuel cell operates at the optimal water level. The fuel cell produces electricity and heat. The PEMFC, DMFC, and SOFC are different types of fuel cells, each with its own characteristics and applications.

difficult to scale-up thick-film technologies to provide cost-effective ceramic multi-cells assembly components with required thicknesses in the range 10–30 µm. Usually, the thick-film electrolyte has to be sintered at temperatures approaching 1,400 °C; this requires a porous ceramic substrate, which is often the anode/cathode material. The substrate material had to be carefully selected to avoid reaction with the electrolyte, and/or thermal expansion mismatch, during the high-temperature sintering process. The incorporation of a relatively weak, brittle structural component in SOFC stacks is at present restricting the application of SOFC systems to those situations that do not demand rapid temperature fluctuations. In this respect the recent development¹ of sintering procedures below 1,000 °C, which should allow the use of metal substrates, represents a significant advance that will enable the development of more rugged SOFC systems.

Another important component in a fuel-cell stack is the impermeable electronic conducting bipolar plate. This has the dual function of distributing the fuel and air to the anode and cathode, respectively, as well as providing the electrical contact between adjacent cells. The corrosive acidic conditions prevailing in the PEMFC and PAFC systems severely restrict the choice of bipolar plate material and at present graphite is usually selected. However, alternative materials or manufacturing methods are mandatory if these systems are ever to satisfy the target cost. Major research and development (R&D) programmes are examining the behaviour of alternative carbon-based materials produced by injection moulding, or coated bilayers (steel). For the high-temperature systems (DMFC and SOFC) operating in the temperature range 500–750 °C, appropriate stainless steel compositions can be specified which meet to satisfy the technical and economic constraints. But for SOFCs operating at higher temperatures (800–1,000 °C), alternative, more expensive bipolar plate materials have to be specified, which at present incur significant cost penalties.

Additional constraints influencing material selection arise from reliability and durability issues. For transport applications, minimal values of performance degradation (for example, 0.1% over 1,000 h) are required for projected operational lifetimes of 5,000 h. But for stationary applications—for example, distributed CHP (combined heat and power) systems—a similar degradation rate must extend over a period of at least 40,000 h (5 years). These different lifetime targets seem to be hindering problems for PEMFC prototype CHP systems, as the stack components were developed originally for transport applications.

A fuel-cell system also incorporates relevant balance-of-plant items such as pumps, valves, heat exchangers and piping. Although these important components contribute at least half the cost of a fuel-cell system, we will not consider them further here, except to note that for the PAFC system, many of which have now been operated for periods approaching 30,000 h, the real source of system breakdown has been balance-of-plant items. External fuel processors (reformers) are also the subject of intensive development around the world, and a variety of innovative compact reformers using diffusion-located pre-reformers, components or micro-channel designs² also illustrate the impact of materials technology on this aspect of fuel-cell systems.

For more than four decades now, reliable, efficient, fuel-cell systems incorporating AFC stacks have proved their worth in the Apollo spacecraft and space shuttles. Excellent electrode kinetics, when operating on pure hydrogen and oxygen, are an attractive feature of this system. But for terrestrial applications, the additional economic restraints, which include the need to replace hydrogen by cheaper hydrocarbon or alcohol fuels, have provided severe problems for materials selection and the associated fuel-processing technology. After 30 years development, the Enasco consortium abandoned attempts in 1988 to develop a fuel-powered by an AFC system. Although Enasco have purchased the technical rights, it is recognized that the full potential of AFC systems will be realized in spite of a current plateau³ hindering the use of AFC systems with commercial fuels.

Approximately 200 PAFC cogeneration units (Intermational Fuel Cells (IFC) FC25, 250 kW) have been installed around the world, and have exhibited excellent reliability. However, the commercial failure of this system is possibly in jeopardy as the manufacturers (IFC and Japanese companies) have been unable to reduce the capital cost sufficiently below US\$3,000 per kW, as originally forecast⁴. Most observers⁵ believe that for initial market entry the target cost per kW must be reduced to around US\$1,000 per kW, falling to below US\$500 per kW with volume production. Accordingly, we focus here on materials aspects of the PEMFC, MCFC and SOFC systems, which at present still appear to present opportunities to exploit their potential.

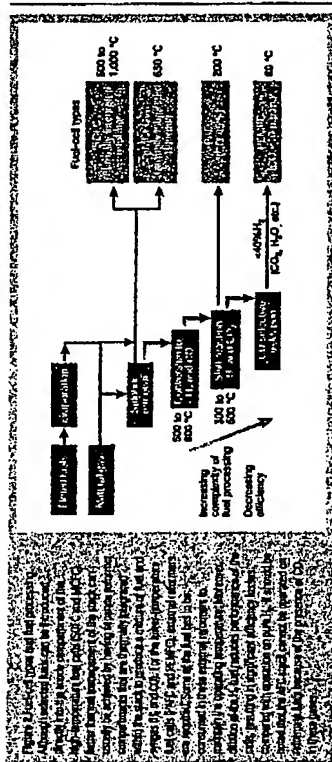
It is important to note that the materials currently being used in PEMFC, MCFC and tubular SOFC prototype demonstration units essentially remain the same as those selected at least 25 years ago⁶. Although innovative fabrication and processing routes have improved the attributes (for example, lower cost and lower Pt loadings) of these materials, it is only in the past five years that system engineering and commercialization issues have highlighted the inadequacies of some of the materials originally selected. As indicated in the next two sections, it is these issues that are now driving the development of alternative materials, particularly for the PEMFC and intermediate temperature (IT)-SOFC stacks.

Polymer-electrolyte-membrane fuel cells

The most important materials under development for PEMFC stacks are construction materials for the end frames, bipolar plates, electrocatalysts for the fuel and air electrodes, and the ion conducting membrane.

Depending on the fuel to be used in the PEM cell, the requirements for these materials are completely different. The simplest case is the operation with pure hydrogen and oxygen or air. Cells with high

Insight review articles



power density and very low degradation are already state of the art. The main requirement for the future is to achieve reduction in the capital cost of the system by attention to materials selection and fabrication, and thereby scaling up the production volume. This target will probably cause a complete review of all the materials used up to now.

The second possibility is to operate the PEM cell with a reformer fuel. In that case, hydrogen and CO traces are present in the fuel. This is a challenge for the fuel electrode in particular, and a CO-tolerant catalyst is required. The most difficult option is the direct methanol fuel cell (DMFC). The methanol electrode also needs a CO-tolerant catalyst, so advanced CO species are formed during the electro-oxidation of methanol. In addition, the small pore methanol molecules diffuse in a very similar to water and readily permeate through existing membrane materials. This behavior leads to a loss in fuel far ratio in the formation of a mixed potential at the air electrode. The development of innovative membrane materials could remove this disadvantage. As the tolerance to CO by the electrocatalyst is strongly dependent on temperature, an alternative membrane with a better temperature stability is also another

important R&D target. However, an operation temperature above the boiling point of water requires a completely different type of membrane material, as no liquid water will be present under these circumstances for the hydrated protonic-conduction mechanism.

Bipolar plates

Much effort is being expended on the development of cost-effective materials for the bipolar plates. With respect to corrosion resistance, graphite materials are preferred. However, the conductivity of graphite materials is much less than that of metallic materials. Some conductivity values are: C polymers, $\sim 1.5 \text{ cm}^2 \text{ s}^{-1}$; graphite, $10^5 \text{ cm}^2 \text{ s}^{-1}$; gold, $45,000 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$; Fe alloys, $5,300 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$; $2,400 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$. For bipolar plates, polymer/graphite compounds are developed with at least $10^5 \text{ cm}^2 \text{ s}^{-1}$, reducing the resistivity of the bipolar plate well below the resistivity of the membrane. In addition, the fabrication costs of graphite plates incorporating gas-distribution channels are high, making such components too expensive. Moreover, as graphite materials are porous, a binder or resin has to be added to produce the necessary impermeability.

Polymeric materials can be coated more easily and cheaply by hot pressing or injection moulding. Polypropylene, for example, can be mixed with graphite to achieve sufficient electrical conductivity. Higher contents of graphite produce better electrical conductivity values, but the associated mechanical properties become more undesirable as the increased brittleness not only reduces the toughness, but also makes manufacturing more difficult and expensive. Typical carbon contents are optimized (the machining processes in association with optimization of the material).

Another strategy is to use metallic bipolar plates. The gaseous flow structure can easily be fabricated in thin metal foils by pressing, but only a few metals are sufficiently corrosion-resistant in the acidic environment of the membrane. The most promising candidates are stainless steels, or other metallic materials such as titanium (which is platinum-titanium and gold (including gold-plated metals) are too expensive. Stainless steel and gold (including gold-plated metals) are two special (banned) metals. The steel is protected by a passive layer of the carbide, but the noble side becomes contaminated by carbon products.^{1,2,3,4} Steels with catalytic bipolar plates have been developed by Noveck and by Sauerbrey.

The second important problem is associated with the electrocatalyst. For operation with pure hydrogen and air, platinum is the most active material. To reduce the cost, nanoparticles of platinum on a carbon

The overall cell efficiency is given by the equation

$$\eta = \eta_v \eta_e \eta_f$$

where η_v is the Gibbs efficiency, η_e is the voltage efficiency, and η_f is the fraction of fuel used.

$$\eta_v = \frac{\Delta G}{\Delta H} = \frac{E}{E_0}$$

$$\eta_e = \frac{E}{E_0} = \frac{E - E_{oc}}{E_0 - E_{oc}}$$

where E_0 is the open circuit voltage, and E_{oc} is the overpotential of the cell reaction. Thus

$$\eta = \frac{E}{E_0} \left(\frac{E - E_{oc}}{E_0 - E_{oc}} \right) \eta_f$$

E_0 is the gross specific enthalpy of the cell components (electrolyte, anode and cathode). Note that the cell structure is often termed the membrane-electrode assembly (MEA) for PEMFC systems, and positive-electrode-negative (PEN) for SOFC systems.

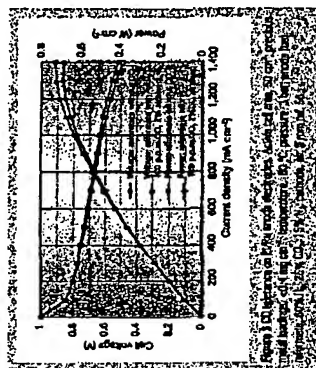


Figure 1. The effect of Pt/C catalyst on the cell voltage. The cell voltage is plotted against the current density. The Pt/C catalyst with a Pt/C catalyst shows a higher voltage at lower current densities, while the Pt/C catalyst with a Pt/C catalyst shows a higher voltage at higher current densities.

support have been developed, and the reduction in noble-metal content without degrading the cell performance has been, and continues to be, an important R&D activity.¹⁰ The platinum loading has been significantly reduced from 2 mg per square centimeter of electrode to values below 0.5 mg cm⁻² without significant impact on performance and lifetime. In the laboratory, even lower platinum loadings have been examined.¹¹

For fuels containing traces of CO, or methanol in the DMFC, a CO-tolerant catalyst is required. This remains one of the most challenging tasks for the successful development of commercial PEMFC systems.¹² For reformate electrodes as well as for methanol oxidation, the removal of adsorbed CO species is the rate-determining step. The oxidation of adsorbed CO on Pt is slow, and is facilitated by adjacent absorbed OH species. This is the reason why Ru, with its low potential for OH-ads formation, is the most efficient component of the binary catalysts. PtRu and other binary and ternary alloys with these noble metals have been investigated intensively,¹³ and performance values have increased significantly. The loss in performance is usually expressed in mV for a certain CO content of the fuel, and recent publications show promising results, as indicated, for example, in Fig. 3.

Membranes

Although the US General Electric Company (GE) initiated the development of PEMFCs in the 1950s, it was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially Nafion was manufactured for membrane cells used in the production of chlorine (chlor-alkali cells). By 1980, Ballard had overcome many of the engineering problems associated with PEMFC systems, and this had stimulated many groups in the United States and Japan to improve the properties of the original Nafion material.¹⁴ For example, higher ionic conductivities could be obtained by selecting perfluorosulfonic acid copolymers with a short pendant group, and it was realized that gas and nonconductive permeability were other important characteristics that had to be improved.

The following properties of polymers membranes need to be specified for use in fuel cells: (1) high proton conductivity, assembly with base groups (e.g., SO₃H), depending on applications; (2) low gas permeability, depending on applications; (3) high mechanical strength and chemical and thermal stability during the reaction of a suitable polymer (e.g., tetrafluoroethylene) with a suitable monomer (e.g., styrene) which is improved by reinforcement; (4) low gas permeability, which is dependent on material and thickness of the membrane; (5) low DMFC applications low electro-osmotic drag coefficient to reduce methanol crossover.

There is significant interaction between the desired properties of the membrane — high conductivity, low swelling, low gas and

medium permeability, and stability — and the type of backbone polymer, the degree of sulfonation and the nano-phase separation into hydrophilic and hydrophobic domains (for example, high degree of sulfonation usually lead to highly conductive membranes, but also to extreme swelling properties). To satisfy these requirements, different approaches have been examined: sulfonated, perfluorinated materials with¹⁵ and without¹⁶ exocyclic support sulfonated poly(hydrocarbon) acid-base complexes and blends with a surplus of acid basic groups and inorganic-organic composite materials with improved thermal stability and better water-retaining properties.

Because of their PTFE-like backbone and relatively low equivalent weight, Nafion and related materials are a favored option and are commonly used in fuel-cell stacks, but the costs remain high. Therefore, much effort is being applied to the development of cheaper, or, usually fluorine-free, membrane materials. But hydrocarbon or other suffer from an insufficient thermal stability, and to more and more aromatic groups have been introduced into the polymer backbone. Polymers seem to be the most stable molecules among the hydrocarbons. For example, poly(p-phenylene ether sulfone)-based membranes were prepared by sulfonation of commercially available polymers such as Loid and Vistec¹⁷ for high-ionic conductivity. High sulfonation fractions are desirable, but high sulfonation can lead to extreme swelling even at room temperature. Thus, crosslinking of the polymer chains at the sulfonic acid groups can be included in the synthesis steps to overcome the problems of swelling. However, the long-term stability of these sulfonamide crosslinking bridges remains unknown. Alternative crosslinking methods, such as covalent crosslinking and ionic crosslinking by the introduction of polymeric bases (acid-base blend membranes), have also been examined.¹⁸

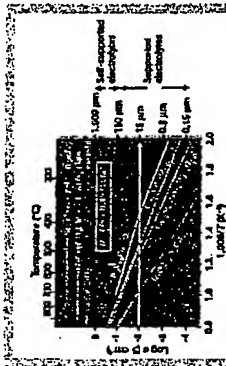
For operation at elevated temperatures, which is desirable for high power density DMFC systems and for reformate fuels with CO levels above 100 ppm, the conduction mechanism becomes the dominant issue. In the types of membranes described earlier (hydrocarbon polymers), the proton-conduction mechanism is based on the migration of hydrated protons. Above 100 °C, pressurized operation is required to ensure the presence of liquid water. Phosphoric acid and polymers with immobilized heterocyclic exhibit a conduction mechanism relying on an anionic diffusion¹⁹, and can be used at temperatures above the boiling point of water. As phosphoric acid in liquid form in a porous matrix is well known from PAFC development, new ways to achieve a composite with better properties have been investigated. One polymer material for high-temperature application is poly(phosphazene) (PPH), which forms adducts with phosphoric acid. Initial publications from Sarrett²⁰ described the use of PPH with phosphoric acid as membrane in fuel-cell experiments. Later developments led to acid-base blend polymers with PPH and sulfonated poly(etheretherketone). Reduced methanol permeability and performance data comparable to that of Nafion 117 have been reported.²¹ Aduis (part of the Hoechst Celanese group) announced the manufacture of PPH-based membrane materials, but only in exclusive cooperation with permen (Purig Power and Hoescht). It should be emphasized that if an alternative membrane material does emerge, considerable R&D will still be necessary to optimize and manufacture the new membrane-electrode assembly (MEA). This development has taken many years for Nafion-type MEAs, although some of the expertise gained may be able to be transferred to the new system.

Fuel cells operating at elevated temperatures

In contrast to other fuel-cell types a SOFC stack can, in principle, be designed to operate within a wide temperature range (500–1,000 °C). It is necessary, therefore, to select the desired temperature of operation. This, in turn, is influenced by the specific application, the type of fuel and the properties of suitable solid electrolytes. For example,

If the SOFC stack is to be integrated with a gas turbine, then system requirements indicate that the temperature of the exhaust gas from the stack should exceed about 850°C. The steam reformer of fuels such as diesel, petrol and propane to produce H_2 and CO gases for the anode inlet, at present, requires preheating to temperatures of 700°C. But it is the properties of the solid electrolyte that present the biggest influence on stack design and materials selection, as highlighted earlier.

Figure 3 summarizes how the specific heat conductivity of the self-assembled thin dielectric layers varies with the sequence of temperatures. By taking a typical value of 0.15 J/cm² for the matrix ASR material, it is possible to estimate the material thickness allowed for a given dielectric component. For example, a device configuration that has specified a self-assembled (~150 nm) nitride-antiferroelectric (N2E) configuration would require a temperature of operation greater than 850 °C. Operation at 850 °C poses major problems for planar devices. The 300 °C configuration compared to (nitride) configurations for example, in the Si/SiO₂-Wettable arrangement. These include stability of the electrode-dielectric interface, the selection of the hydroxide-rich material, and the optimal material thickness. The 300 °C configuration is more likely to be necessary to planar 300 °C stacks, the wafer-level defects are still enough, allow

[illegible][illegible]

insufficient reaction between the MSF cathode and electrolyte. Selection of the cathode (MSF) and anode (VSE) compounds was established during the 1970s by Westinghouse and ABB, after examining a variety of oxide compounds for long-term compatibility with YSZ at elevated temperatures. This complex combination was later mentioned in terms of two "stable" thermoelectrical data¹¹

The Siemens-Westinghouse fiberoptic design renders the most developed SOPC present, and has been evaluated in units generating 25 MW, 100 MW and 200 MW. More recently 200-MW units have been developed with microcircuits to provide a system capable of generating power with an efficiency of 80% and a capacity for generating electricity around 80% efficiency. Large, multi-megawatt microintegrated systems are predicted to produce electricity as efficiently as conventional systems, approaching 100%. However, these advances are more concerned with the use of system design rather than the selection and development of various system design blocks.

thermochemical vapourization side-side fuel cells. The worldwide production of gas turbine-based companies (such as General Electric, GE and IBM) and the development of multi-fuelled engines (such as the new engines of the Boeing 747) has led to a growing interest in the development of SOFCs, which are being used for stationary power plants. In the last few decades from 1970, by 1980, however, the technology has been recognized that for smaller SOFC stacks, such as those being used for portable power, the cost of the manufacturing process is the major factor for the development of these stacks. The use of SOFCs as power is also being considered by IBM units to improve stand-by power for distributed (distributed by fiber-optics) communication and distributed supply plants. In addition, many automotive manufacturers are examining, whether small SOFC stacks (3-5 kW) can be developed to supply the electrical power for auxiliary functions such as air conditioning in vehicles.

Examples of the most important results are presented in Table I. The first two rows show the effect of the temperature on the rate of polymerization of the monomer. The polymerization of the monomer at 100°C. is very slow, and the rate of polymerization at 150°C. is about 10 times faster. The rate of polymerization at 200°C. is about 100 times faster. The rate of polymerization at 250°C. is about 1000 times faster. The rate of polymerization at 300°C. is about 10000 times faster. The rate of polymerization at 350°C. is about 100000 times faster. The rate of polymerization at 400°C. is about 1000000 times faster. The rate of polymerization at 450°C. is about 10000000 times faster. The rate of polymerization at 500°C. is about 100000000 times faster. The rate of polymerization at 550°C. is about 1000000000 times faster. The rate of polymerization at 600°C. is about 10000000000 times faster. The rate of polymerization at 650°C. is about 100000000000 times faster. The rate of polymerization at 700°C. is about 1000000000000 times faster. The rate of polymerization at 750°C. is about 10000000000000 times faster. The rate of polymerization at 800°C. is about 100000000000000 times faster. The rate of polymerization at 850°C. is about 1000000000000000 times faster. The rate of polymerization at 900°C. is about 10000000000000000 times faster. The rate of polymerization at 950°C. is about 100000000000000000 times faster. The rate of polymerization at 1000°C. is about 1000000000000000000 times faster.

Anti-SOFC configuration that seeks to retain the specific advantage of both the tubular and planar arrangements is being developed by Calsonic. This integrated planar-stack concept, incorporated by Calsonic, is a multi-cell assembler connected in series and supported by a ceramic substrate, and has many similar features to the original Westinghouse tubular design.

Most desorbents must not poison Ti-SiO₂ systems (as involved in the thermal-expansion VSE electrolysis), and so fit most groups (we must disregard (N₂-N₂) VSE electrolysis), which allow the electrolytic powder to be stirred for 60 sec in fluid around 1,000°C. One of the problems associated with using porous, composite N₂-VSE anodes is that they rely heavily on the porous structure for thermal-expansion compatibility with the VSE block itself. Accordingly, several groups are examining porous electrolytic materials, such as (N₂-N₂) VSE, (N₂-N₂) VSE and/or desorbents, with their interfacial anode in the porous electrolytic material. This approach may be useful for the regions near the Ti-SiO₂ interface. The use of the VSE can provide better thermal-expansion compatibility, problems still remain over the volume change associated

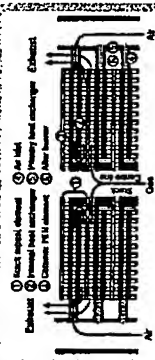


Figure 1. Schematic diagram of a solid oxide fuel cell (SOFC) stack. The stack is composed of multiple cells, each with a cathode, electrolyte, and anode. The diagram illustrates the flow of gases and the electrical output of the stack.

with the reduction and oxidation of the Ni component. As the porous substrate-electrolyte film is usually coated in air around 1,400°C, nickel is present as NiO, which has to be reduced by the fuel during the initial 'heating' cycle of the assembled stack. Additionally, operating procedures have to be designed to prevent the use of fuel flowing through the stack at temperatures below the start-up temperature, which is around 800°C, to avoid the formation of nickel carbonyl, a highly volatile and toxic compound. The start-up temperature is determined by the rate of the energy input to the system.

Many SOFC developers are using metallic bipolar plates. Often a ferritic stainless steel is specified because of the low ($12.5 \times 10^{-3} \text{ K}^{-1}$) thermal-expansion coefficient of these alloys. Moreover, by using compositions stabilised with Ni-Ti, excellent electrocatalytic characteristics can be maintained between the cell components for extended periods. Providing appropriate precautions are followed, many R&D laboratories have reported good performance values for Ti-SOFC stacks incorporating the following positive electrolyte-negative (PEN) component, anode-supported (AS) thin YSZ electrolyte, LSM-YSZ cathodes, and stainless steel bipolar plates.

To minimise sealing requirements, many Ti-SOFC stacks have adopted a circular design in which the fuel and air are introduced by means of an appropriate manifold at the centre of the PEN structure. Arrangements are made to distribute the air and fuel gases over the cathode and anode, and the flow rates are adjusted to ensure almost complete conversion of the fuel by the time it reaches the stack periphery. Unreacted fuel and air are then combusted without large temperature changes. These design features minimise sealing problems and slow thermal cycling. Examples are provided by the Shaker Fuel Micro-Cell Corporation designed for residential microcombined cycle (MCHP) and the auxiliary power unit (APU) prototype (Fig. 6) constructed by the Döhlitz-MKW-Global Thermoelectric Corporation for incorporation into vehicles. Due to the high thermal conductivity of the ceramic electrolyte, the heat loss during the heating and cooling rates cannot exceed $\sim 500^\circ\text{C}$ per hour, owing to the development of stresses associated with thermal-expansion mismatch, and to the brittle glass and ceramic sealants. Although the thermal shock resistance of the ceramic electrolyte may not be too severe for large (100 kW) stacks, the thermal shock resistance of the ceramic electrolyte is still required to maintain the integrity of the stack. Commercial units may be expected in the next few years, and the technology and materials (e.g. 1,100 kW) have been effectively demonstrated.

Ti-SOFC stacks incorporating alternative sequences. Although YSZ is still the dominant electrolyte material for SOFC stacks, selection of this material is not without problems and research

continues into the long-term evolution of ceramic-based ZrO₂-YSZ material.

In principle, the use of ceramic electrolytes such as CGO should allow the cell operating temperature to be lowered to around 500°C (see Fig. 4). But potential problems associated with PEN structures incorporating ceramic electrolytes have restricted investment in this technology. It is well known that, at elevated temperatures, Co^{2+} ions can be reduced to Co^{0} under fuel-rich conditions, resulting in the anode component of the associated electronic conductivity (and dependent lattice composition) produces an internal short circuit in the PEN stacks, which can significantly degrade the efficiency and performance of cells. However, if the operating temperature is lowered to around 500°C, then the electronic conductivity is small, and carbon neglected under typical operating conditions of the engine.

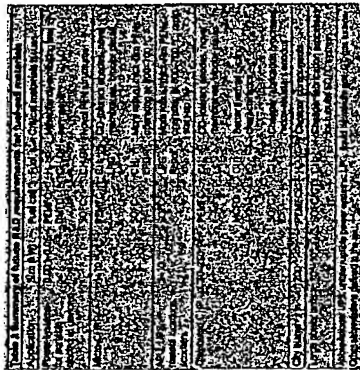
Another difficulty is that the reduced expansion of the attractive properties of CGO at 500°C has been the need to develop alternative ceramic components that function effectively at lower temperatures. Recent developments in this area have been reviewed by Jodanis *et al.*¹⁰ and there are indications that appropriate materials for ceramic cathodes can be fabricated which exhibit small thermal-expansion coefficients (e.g. $15.5 \text{ V} \text{ at } 1 \text{ A cm}^{-2}$). Ceramic stacks such as Ni-CGO also provide adequate performance at 500°C for stationary power plants, indicating that Ti-SOFC stacks at 500°C are now a viable option.

Operation at intermediate temperatures is also an advantage. R&D effort has been made to develop alternative materials to replace the established Ni-YSZ anode. One strategy is to develop electronic conducting oxides that are stable under the use of H_2 . This material can catalyse carbon deposition under certain operating conditions, and also form NiO , which is accompanied by a 'deactivation' volume expansion, when the anode is exposed to a mixture of hydrocarbons. Another approach is to combine with the identification of alternative oxides that allow the direct oxidation of hydrocarbons. The challenge is to find 'reactive' materials that are 'stable' under the conditions of the engine, but there is little doubt that this topic will remain a fruitful area for further investigations.

Operation at 800°C allows the use of cheap high-temperature glasses in place of rigid, brittle glass or ceramic seals, thus permitting greater design flexibility for the stack configuration. At Imperial College, London, researchers have taken advantage of the fact that the thermal-expansion coefficient of CGO and ferritic stainless steel are virtually identical ($12.5 \times 10^{-3} \text{ K}^{-1}$), so that the thick-film PEN structures can be supported on a porous stainless steel substrate. These metal-supported PEN structures are robust, and should withstand the rapid temperature cycles expected during operation of small Ti-SOFC stacks.

Another electrolyte, doped LaCoO_3 (LSCM), is also attracting much attention for Ti-SOFC applications. Although its conductivity is slightly smaller (see Fig. 5) than CGO at 500°C, it is more stable in air and it could be more appropriate to use the electrolyte at temperatures around 600°C, where the reduction of Co^{2+} in CGO becomes significant. It has been difficult to fabricate pure single-phase ceramic electrolytes, and second phases such as SrLaCoO_{3-x} and LaCoO_{3-x} are often detected in the grain boundaries. Whether these phases are responsible for the enhanced reactivity of LSCM, or whether it is an inherent property of LSCM, are questions that require urgent research. Moreover, the preferred composition, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_{3-x}$, does not seem to be the most appropriate for practical applications. Although the presence of a second phase is not a problem for the synthesis of alternative oxygen-ion conducting electrolytes, it has proved difficult to prepare a single-phase material with an appropriate combination of properties that can replace the traditional ceramic electrolytes (e.g. ZrO_2 and CGO).

Experiments involving single-component SOFC fuel cells have been reported. In this configuration a mixture of the fuel and air flows



per-head performance. This, for example, is the strategy adopted recently by the US Department of Energy for the Solid State Energy Conversion Alliance, which aims to mass produce 5-W SOFC modular stacks with a target cost of US\$400 per kW. Once this small-scale technology has demonstrated its reliability and cost target, then larger units based on the same technology can be expected to penetrate other sectors of the stationary power and transport markets.

Another area receiving increased attention is the development of fuel-cell power sources for a variety of portable electronic devices. As batteries struggle to keep up with the specific power demands of mobile devices, innovative DMFC designs¹⁰, fabricated using techniques developed for the semiconductor industry, promise energy densities that are between three and five times better than current lithium-ion batteries. The high power margins and relatively low power demands (~1 W for transmission) associated with cellular telephones, for example, could provide a useful market entry for these small fuel cells, particularly for hybrid systems.

1. Goren, M. V. Ch. 10. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 101-110 (1999).
2. Sauer, J. C. H. Ch. 11. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 111-120 (1999).
3. Sauer, J. C. H. Ch. 12. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 121-130 (1999).
4. Sauer, J. C. H. Ch. 13. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 131-140 (1999).
5. Sauer, J. C. H. Ch. 14. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 141-150 (1999).
6. Sauer, J. C. H. Ch. 15. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 151-160 (1999).
7. Sauer, J. C. H. Ch. 16. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 161-170 (1999).
8. Sauer, J. C. H. Ch. 17. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 171-180 (1999).
9. Sauer, J. C. H. Ch. 18. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 181-190 (1999).
10. Sauer, J. C. H. Ch. 19. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 191-200 (1999).

11. Sauer, J. C. H. Ch. 20. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 201-210 (1999).
12. Sauer, J. C. H. Ch. 21. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 211-220 (1999).
13. Sauer, J. C. H. Ch. 22. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 221-230 (1999).
14. Sauer, J. C. H. Ch. 23. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 231-240 (1999).
15. Sauer, J. C. H. Ch. 24. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 241-250 (1999).
16. Sauer, J. C. H. Ch. 25. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 251-260 (1999).
17. Sauer, J. C. H. Ch. 26. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 261-270 (1999).
18. Sauer, J. C. H. Ch. 27. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 271-280 (1999).
19. Sauer, J. C. H. Ch. 28. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 281-290 (1999).
20. Sauer, J. C. H. Ch. 29. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 291-300 (1999).
21. Sauer, J. C. H. Ch. 30. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 301-310 (1999).
22. Sauer, J. C. H. Ch. 31. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 311-320 (1999).
23. Sauer, J. C. H. Ch. 32. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 321-330 (1999).
24. Sauer, J. C. H. Ch. 33. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 331-340 (1999).
25. Sauer, J. C. H. Ch. 34. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 341-350 (1999).
26. Sauer, J. C. H. Ch. 35. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 351-360 (1999).
27. Sauer, J. C. H. Ch. 36. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 361-370 (1999).
28. Sauer, J. C. H. Ch. 37. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 371-380 (1999).
29. Sauer, J. C. H. Ch. 38. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 381-390 (1999).
30. Sauer, J. C. H. Ch. 39. Fuel cells and the development of portable electronic devices. *Fuel Cells*, Vol. 1, pp. 391-400 (1999).

insight review articles

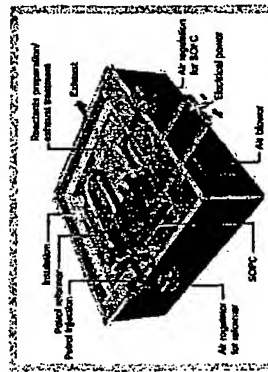


over both electrodes of a ceramic cell. One electrode is porous an anion-exchange polymer for the reduction of oxygen, whereas the second electrode is designed to catalyze the fuel oxidation. This configuration allows the use of a solid electrolyte and anion-exchange polymer electrolyte (PEM) without the need for a liquid electrolyte. But the published design is not intended to be a final design. The fuel cell electrodes also catalyze the external oxidation of the fuel. The heat generated by these surface reactions can significantly raise the temperature of small samples so that the reported data probably refer to T_c values around 100°C higher than those stated. Parallel chemical oxidation of the fuel will of course significantly reduce the overall system efficiency, and technological realization of this configuration seems unlikely.

Very high performance has been claimed¹⁰ at 500°C using cupro-nitric electrolyte incorporating CO and methanol fuels. But the long-term stability of such mixtures in a fuel-cell environment must be established and these claims require further independent scrutiny.

Investigations also continue into ceramic proton conductors. The composition $BaZr_{0.9}V_{0.1}O_{3-x}$ for example can exhibit a protonic conductivity that approaches the oxygen-ion conductivity of COO at 500°C (that is, $10^{-3} \text{ S cm}^{-1}$). But this is the theoretical conductivity; ceramic proton conductors will not be able to electrochemically oxidize CO and do not, at present, appear to offer any advantages over the oxygen-ion conducting electrolytes. In this temperature region, interesting results have also been reported¹¹ for the solid acid CaHSO_4 at 150°C. Ceramic protonic conductors are more likely to be exploited in chemical engineering applications requiring the separation and generation of hydrogen.

Molten-carbonate fuel cells
Although the materials (Table 1) used for MCFC stack components have essentially remained unchanged over the past 25 years, significant developments in fabrication technology were introduced during the 1980s. Cost-effective tape-casting techniques now allow the intermediate electrolyte matrix to be manufactured up to a size of 1 m². These manufacturing advances were important as the power



density of MCFC systems operating at 650°C is relatively low (~150 mW cm⁻²), requiring large cell areas to be fabricated. The requirement for intermediate CO₂ from the anode exhaust to the cathode to maintain the composition of the carbonate electrolyte also complicates the balance-of-plant equipment. It follows that the MCFC is only likely to be commercialized only at sizes greater than 100 kW, and originally MCFC plants were considered as large (condensing) combined-cycle power stations.

To develop user interest it was considered that large plants should be demonstrated as soon as possible, and this led to the construction in the United States of the 1.4-MW Sinochem system by Energy Research Corporation. Although completed in April 1994, evaluation of the plant had to be postponed owing to problems with the material selected for the stack external manifold. It is now believed that a more appropriate strategy is to develop smaller MCFC systems (~250 kW) for distributed CHP applications using natural gas. An example of this approach is provided by the 300-kW 'Hot Module' unit, developed by MTU Friedrichshafen (a subsidiary of DaimlerChrysler AG), and it is encouraging to note that the first demonstration module has already been operated successfully for more than 1 year (8,000 h) at an electrical efficiency of 47%. Because of the corrosive nature of the molten salt $\text{Li}/\text{Na}/\text{KCO}_3$ electrolyte, lifetime issues have always been of concern for the MCFC system. However, a recent update¹² suggests that most components should attain the target value of 40,000 h, except possibly the coating used to protect the anode structure, which remains the focus of further materials development.

Operating procedures for MCFC systems are influenced by limitations associated with two of the components. In cooling down the hot stack in the absence of a fuel supply, it is necessary to protect the Ni-Cr anode from oxidation by the introduction of an inert gas into the anode compartment. Moreover, however, is the inability of the immobilized electrolyte matrix to withstand more than 2 to 5 thermal cycles through the melting point of the molten salt electrolyte. Thus, during stand-by situations the temperature of the MCFC stack must be maintained high enough to prevent solidification of the molten salt electrolyte. Clearly both the MCFC and SOFC systems will initially be competing for the same sub-megawatt CHP market sector. It is expected that both will operate at similar electrical efficiencies, and so the cost of the installed plant will determine which technology eventually has the largest market penetration. It is also interesting to note that both fuel-cell types require procedures to prevent redox reactions damaging the anode, and to restrict thermal cycling of the plant during abnormal operating situations.

Conclusions

Probable applications of fuel cells in the next decade together with a selection of critical materials issues are summarized in Table 2. It is recognized that the capital costs (0.553,000–10,000 per kW) of prototype fuel-cell systems are too high. Although volume production can be expected to reduce these costs, it may be difficult to obtain sufficient market share to justify the investment for mass production while competing against established technology. Although significant niche markets exist, such as the PEMFC system for city buses, many observers believe that a more appropriate strategy is to target those sectors of the market (for example, 1–10 MW generation) where the existing technology is inefficient and displays extremely poor

Spar Plug use alumina since it is electrically insulator:

APPENDIX E

<http://yshsp.en.alibaba.com/search/offer>

Auto Ignition System use alumina since it is an insulator:

<http://starsparkplug.en.alibaba.com/offerlist.html>

Alumina insulating coating:

<http://www.freepatentsonline.com/6844023.html>

Shanghai Morgan Matroc Technical Ceramics Co.,Ltd

High efficiency alumina heat-electric Insulator for welding and heat treatment. Morgan Technical Ceramics Shanghai produces a complete range of ceramic ...
www.morganmatrocsh.com/e_chanpin_7.htm - 15k - [Cached](#) - [Similar pages](#)

Ortech industry -table containing alumina 's properties:

<http://www.ortechceramics.com/alumina.htm>

Ceramic Tube and Ceramic Rod Products - (111 companies)

Ceramic tube and ceramic rod products are suitable for use in applications requiring high temperature strength, erosion resistance, electrical or thermal insulation, and other specialized characteristics. [Search by Specification](#) | [Learn more about Ceramic Tube and Ceramic Rod Products](#)

Alumina Insulator:

<http://www.prgtech.com/engineering.html>

Alumina use in thermocouple assembly as a insulator:

PDF Noble Metal

File Format: PDF/Adobe Acrobat
elements, elements with Insulators or assemblies. A typical. assembly includes a head, alumina Insulators and a protecting ...
www.watlow.com/literature/specsheets/files/sensors/ricnom0305.pdf - [Similar pages](#)

Page 8 -shows use of alumina tube in an assembly as a Insulator:

Henry Rohrs poster

File Format: PDF/Adobe Acrobat
Alumina Insulator. Nickel Seat. Gold O-Ring. SS O-Ring Seat. Vespel Support. Sapphire Ball. PZT Bimorph. Pulsed Valve. The pulsed valve consists of a ...
www.chemistry.wustl.edu/~msf/ASMS98/Pshenry98.pdf - [Similar pages](#)

Goodfellow- a table listing volume resistivity of alumina $>10^{14}$ ohm-cm.:

<http://www.azom.com/details.asp?ArticleID=2103>

APPENDIX F

There are no related appeals, interferences, or judicial proceedings.